Ultraviolet bleaching and regeneration of ·Si≡Si₃ centers at the Si/SiO₂ interface of thinly oxidized silicon wafers

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The ·Si≡Si₃ defect revealed by electron spin resonance (ESR) at the Si/SiO₂ interface has been found to be very sensitive to ultraviolet (UV) radiation at 2537 A. With native oxides or very thin thermal oxides, UV bleached the signal, which then recovered slowly in room temperature air, or rapidly upon water immersion. Details of the bleaching suggest outer-oxide surface trapping by adsorbed oxygen, rather than bulk oxide traps. In HF-stripped silicon, an opposite UV effect was observed, i.e., an accelerated growth of ·Si≡Si₃ centers. The physico-chemical responses of ·Si≡Si₃ reflected several stages in the development of nascent oxides on silicon wafers. The UV trapping phenomenon further offers a potential method for determination of the energy levels of the ·Si≡Si₃ defect, and thus for clarification of its role in interface trapping.

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INTRODUCTION

The apparent demonstration of ·Si≡Si₃ centers at the Si/SiO₂ interface by electron spin resonance (ESR) offers a basis for improved study of charge traps in metal-oxide-silicon structures. A good quantitative correlation of ·Si≡Si₃ concentration with interface trap density D_{it} has been observed in chemically diverse samples.[1] Nonetheless, attempts to demonstrate the direct electrical control of ·Si≡Si₃ electron occupancy have been inconclusive.[2] An alternative approach, variation of trap occupancy with Fermi level shift in a series of samples with graded resistivity, has not yet been possible because of ESR limitation at the required high dopant concentration. Preliminary attempts to change the occupancy with visible light, and thereby deduce trap energy, have been obscured by confusing side effects of carrier generation.[3] Recent very pertinent experiments showing elimination of the ·Si≡Si₃ signal by positive or negative corona oxide charging offer new hope for controlled voltage effects.[4] The experimental problems, however, associated with each of these approaches suggest seeking alternative methods for defining the nature and energy of the ·Si≡Si₃ centers.

Ultraviolet (UV) irradiation of Si/SiO₂ structures has previously been employed to study photoemission from the silicon valence band into the Si/SiO₂ conduction band.[5] Injection of UV photoemission electrons has in turn been used to probe trapping in the nitride region of metal-nitride-oxide-silicon devices.[6] Finally, there is some evidence that UV itself promotes trap formation.[7] In view of these and other studies, UV seemed a promising approach to the characterization of the ·Si≡Si₃ center.

I. EXPERIMENTAL DETAILS

Silicon wafers, (111) orientation, with thermal, native, and assisted room-temperature oxides were used for these experiments. Thermal oxides were grown in a simple quartz-lined furnace; samples were quickly withdrawn in air, and occasionally quenched in water for maximum ·Si≡Si₃ concentration. ESR was performed on one wafer at a time, size 4×20 mm, in a standard Varian E-line Century 9 GHz spectrometer with 1 sec time constant. Optical signal enhancement at 77 °K was often used to improve the signal strength; care was taken to assure that no confusing side effects were introduced.[3] The signals shown here are real time, i.e., not averaged. Ultraviolet irradiation was performed with a number of standard laboratory sources, but usually with a mercury arc and several simple filters to isolate visible, 3660 A, and 2537 A components. Irradiations were performed outside the cavity, since the effects were fairly long lasting. Other details of specific sample treatments are given below, as appropriate.

II. OBSERVED ULTRAVIOLET EFFECTS

It was immediately observed that UV light produced a strong and persistent effect on the ·Si≡Si₃ signal in samples with very thin oxides; however, it did not affect the ESR response of samples with the normal thermal oxides of ~ 1000 A thickness. The UV-affected samples included thin thermal oxides as well as sufficiently mature native oxides. After a few minutes exposure, the ESR signal was drastically reduced. It recovered in several hours at room temperature. A typical bleach and recovery is shown in Fig. 1. A UV-accessed trapping is suggested.

The recovery was greatly accelerated at 373 °K and became almost imperceptibly slow at 77 °K. Recovery was also very slow at 295 °K in a vacuum dessicator. In room ambient, recovery varied considerably between samples, and somewhat on different occasions, but always required several hours. It was possible to restore the signal very quickly (5–10 minutes) by immersion in deionized water. This suggests
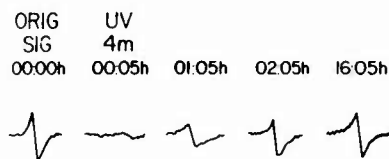
ORIG   UV
SIG   4m
00:00h 00:05h 01:05h 02:05h 16:05h

FIG. 1. Sequential observations on same sample showing UV bleaching of ESR signal from interface ·Si≡Si₃ in a native-oxide silicon wafer and recovery in room ambient. UV exposure 4 minutes; recovery in hours after exposure.

ORIG UV   H₂O   UV   UV   UV   H₂O
SIG   O₂   VAC   N₂   O₂

FIG. 3. UV bleaching in presence of oxygen; lack of bleaching in nitrogen or vacuum. All exposure times approximately 15 min.

discharging or neutralization of trapping centers in the oxide, rather than some effect of penetration of water to the interface. The latter would probably neutralize the signal, as in the case of H_2 anneal or steam oxide growth.

The evident production of ozone by the UV sources raised the possibility that the ·Si≡Si₃ center was neutralized by reaction of ozone with the center. However, exposure of the samples to an ozone generator without UV had no effect whatever on the signal. The observation of ozone effects, together with the water-induced signal restoration, are shown in Fig. 2. Note that normal bleaching, and no more, was observed when the UV light is supplemented by extra ozone. It was further observed, however, that the ambient atmosphere had a critical effect on the UV bleaching, as shown in Fig. 3. Although O_3 per se had no special effect, oxygen or air was necessary for bleaching. No UV effect whatever was observed in either vacuum or nitrogen.

The spectral dependence of the bleaching was crudely determined with filters for selection of visible, 3660 A, or 2537 A radiation. Only the 2537 A line affected the signal, Fig. 4. The need for this 4.9-eV photon suggests that the trapping is preceded by excitation of ·Si≡Si₃ electrons and/or silicon valence electrons to the conduction band of Si/SiO_2.

The observations discussed so far were all made with native oxides. In view of the possible mechanisms of H_2O-aided restoration of the ESR signal, it was of interest to test different thicknesses of oxide. The result is shown in Fig. 5. The strongest bleaching was observed in the native oxide, estimated to be <30 A thick.[8]

The rapid decline in bleaching as a function of oxide thickness suggests a surface effect. Either the ·Si≡Si₃ electrons must tunnel to a surface trap, or the outer surface accumulates a charge whose effect diminishes as the oxide layer thickens. In related tests, several thick oxides grown in steam were tested with or without various annealing treatments in a search for the more familiar bulk oxide trapping ascribed to water-related defects,[9-11] but no detectable effects were seen.

The hypothesis of an outer-surface oxide trap raised the possibility of a role for surface contaminants. Since it is known that short-wave UV is used in quartz-crystal processing to eliminate carbonaceous surface contamination, we examined the possibility that such a mechanism might provide or activate potential trapping sites. A number of considerations ruled this out, in particular the fact that the UV bleaching effect was not altered when the surface was very heavily coated with various organic substances—so heavily that it was impossible for UV cleaning to take place.

The result for oxides thicker than native suggested extension to the regime below native, i.e., from bare silicon to mature native oxide, <30 A. Samples were prepared for this study by removal of oxide in HF followed by immediate insertion into the ESR cavity. (Since our etch was crudely performed in room ambient, the silicon does not long remain in the bare condition, but nonetheless is "bare" from an ESR standpoint). There was no signal at all for this "bare" silicon surface. Truly bare silicon exposed to air quickly grows native oxide. However, it required several days for the ·Si≡Si₃

ORIG   O₃   UV   H₂O   UV
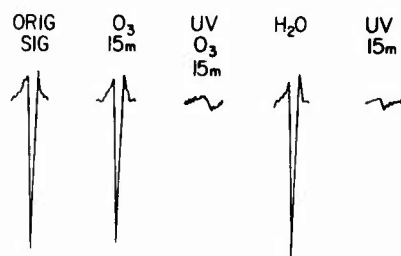SIG   15m   O₃   15m
              15m

FIG. 2. Lack of ozone effect on UV bleaching and rapid signal recovery by water immersion. Exposure to different ambients in immediate succession for times shown. Water immersion time not closely controlled; usually 5–10 minutes. Air always present.
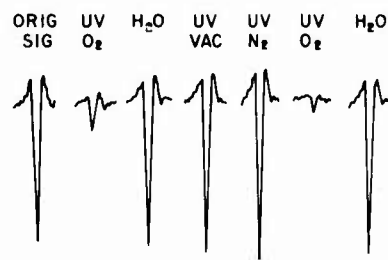
ORIG WHITE 3660   ORIG 2537 2537
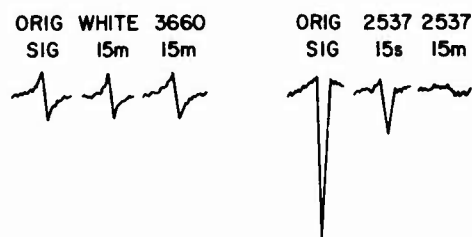SIG   15m   15m   SIG   15s   15m

FIG. 4. UV bleaching produced by 2537 Å radiation; lack of bleaching with 3660 Å or visible light. Three signals on left side are all small because no optical enhancement was used (see text).
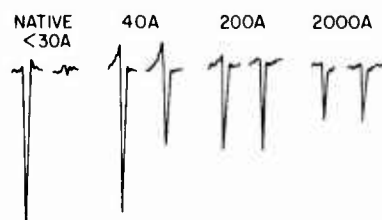
NATIVE   40A   200A   2000A
<30A

FIG. 5. Decline of UV bleaching with oxide thickness.

signal to reappear, asymptotically approaching some limit. The effects of UV on the ESR of this nascent oxide regime were quite unexpected. Exposure of the freshly etched silicon to UV in air, but not in vacuum, resulted in very rapid reappearance and growth of the $\cdot$Si$\equiv$Si$_3$ centers, i.e., in a few minutes, which is just the reverse of the bleaching effect observed with thicker oxides. In the case of H_2O the effect is also reversed; immersion in water in the nascent oxide regime eliminated the $\cdot$Si$\equiv$Si$_3$ signal. In continuation of the experiment, either by repeated UV dose, or by extended exposure to room-temperature air, the system eventually re-

ORIG   UV   HF   UV   UV
SIG   VAC   VAC   AIR
        10m   10m   15m

ORIG   HF   UV H_2O 2WKS   UV H_2O
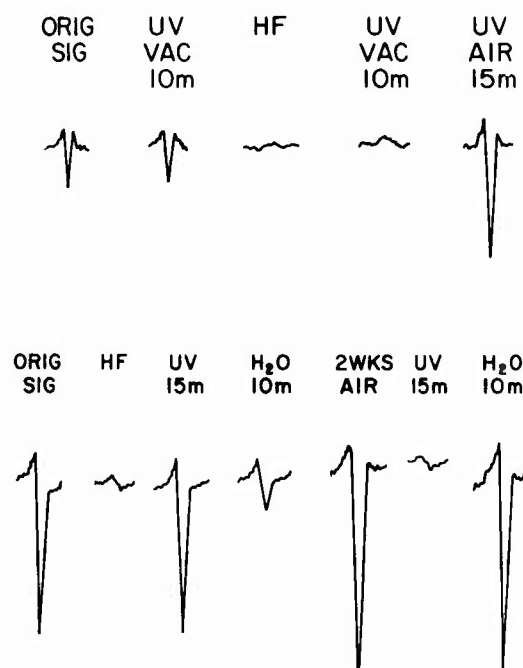SIG   15m   10m   AIR   15m   10m

FIG. 6. Top sequence: rapid regrowth of oxide induced by UV after HF etch and absence of UV-bleaching effect with nascent oxide. Bottom sequence: UV-accelerated oxidation and absence of UV bleaching in nascent oxide; annealing of $\cdot$Si$\equiv$Si$_3$ by water in nascent oxide; return of bleaching in mature native oxide; return of signal recovery by water immersion in mature native oxide. UV exposures in air in bottom sequence.

verted to the condition described earlier in the paper. The UV again bleached the $\cdot$Si$\equiv$Si$_3$ center and H_2O restored it. The nascent oxide observations are portrayed in Fig. 6.

III. DISCUSSION AND PROPOSED MODEL

A consideration of all the various features of the UV experiments suggests very strongly the occurrence of the well-known oxygen adsorption phenomenon. Oxygen is readily adsorbed on the bare surface of n-type semiconductors because of its high electron affinity.[12] It can attract electrons from the conduction band to form O_2^-, and thus produces a stable double layer, with a depleted or inverted semiconductor surface as the other member. There are numerous variations in this oxygen adsorption phenomenon.[13] Adsorption on bare semiconductors may require a photon assist, or be enhanced by photons, depending on specific circumstances—availability of conduction electrons, relative energy levels, etc. In the case of our oxidized Si, UV photons are essential to establishment of the observed charge balance, although details of the intermediate mechanisms cannot be discerned from the evidence at hand. The 4.9-eV photon has ample energy to raise valence electrons to the conduction band of the SiO_2.[5] Once there, the electrons travel easily to the nearest O_2 molecule, forming O_2^-. The accumulating negative charge on the oxide surface ultimately bends the energy bands in SiO_2 and Si so far that the $\cdot$Si$\equiv$Si$_3$ centers are above the Fermi level and are depopulated, forming $^+$Si$\equiv$Si$_3$, invisible to ESR.

The proposed mechanism is shown in Fig. 7. A steady state is attained when charging of the surface has tilted the SiO_2 bands so much that the UV-stimulated electrons can no longer surmount the barrier. Possible tunneling from the charged surface back through the oxide to the silicon also might influence the final balance. It is possible that $\cdot$Si$\equiv$Si$_3$
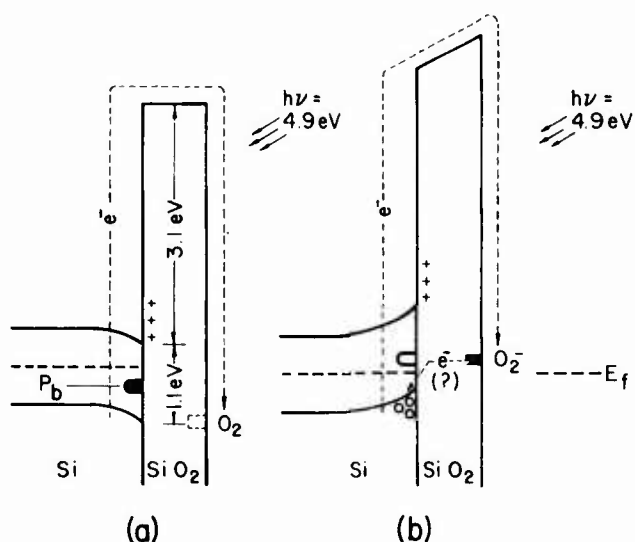

FIG. 7. Proposed oxygen photosorption mechanism for UV bleaching of $\cdot$Si$\equiv$Si$_3$ centers.

electrons are ejected by the direct effect of the UV, but this would not be readily distinguishable without a better selection of light sources. The final observed result would be the same, whether $\cdot$Si$\equiv$Si$_3$ electrons or Si valence electrons are directly excited, or both.

A rough calculation will show the expected concentration of the charges and the resultant potentials. The energy from the valence band of Si to the conduction band of SiO_2 is 4.2 eV. Thus 2537 A light has 0.7 eV more energy than required, and this excess determines the final upward tilt of the SiO_2 bands in steady state. The capacitance between SiO_2 surface and the silicon surface is

$$C = \chi\epsilon_0/a,$$

where a is oxide thickness, χ is dielectric constant of SiO_2, and ϵ_0 is free space permittivity. For a 30-A oxide, $C = 1.3 \times 10^{-2} fm^{-2}$. The magnitude of the oxide charge can now be obtained from

$$Q = Nq = CV.$$

We find $N = 6 \times 10^{12}$ cm^{-2}. This is $2X$—$3X$ greater than the maximum observed concentration of $\cdot$Si$\equiv$Si$_3$ centers. The mechanism is thus strong enough to empty the centers as well as to establish a substantial accretion of holes at the interface. The mechanism would, of course, lose potency with thickness, since the surface concentration of charged oxygen will decline for constant V.

Reversal of the bleaching effect by water now seems most likely to be a simple short circuiting of the charged layers, either around the edges of the sample or via pinholes in the oxide. With such short circuiting, the O_2^- electrons could return to the silicon without tunneling through the oxide. The much slower nonimmersion signal recovery may be due to such tunneling, or thermal detrapping, or atmospheric moisture.

The explanation of the inverse UV and water effects in nascent oxides is somewhat more speculative, but several possibilities can be suggested that are consistent with the general model. There are four features to be explained: (1) the lack of an initial signal; (2) the development of a signal upon UV irradiation; (3) the observation that UV does not remove the signal; and (4) the loss of the signal by exposure to water. (1) The lack of an initial signal with the very thin oxide present may be (a) because there is a lack of the fixed oxide charge (N_f) that attracts electrons to fill the $\cdot$Si$\equiv$Si$_3$ centers, (as in the left part of Fig. 7), or it may be (b) because with the thin oxides, the $\cdot$Si$\equiv$Si$_3$ centers, arising as they do from strain between the developed oxide and the substrate silicon, do not exist. (The completely pristine silicon surface is reconstructed to preclude dangling orbitals.[14]) (2) The fact that UV produces the signal in the presence of oxygen then would correspond to the photo-stimulated development of enough oxide[15] either (a) to provide the needed N_f centers or (b) to induce sufficient oxide strain to produce the $\cdot$Si$\equiv$Si$_3$ centers. (3) The observation with thin oxides that the UV does not remove the signal is explained simply by the fact that the UV cannot induce excess oxygen adsorption. When the oxide is thin enough that electrons can tunnel through the oxide both ways between the adsorbate and the silicon, the UV cannot

alter the equilibrium adsorption. Finally, (4) there are three possibilities for the effect of water, which in this thin oxide regime removes the signal. The effect may be due to "plasticizing" the thin oxide and thus removing the strain; it may be due to a neutralization of N_f centers by OH$^-$; or it may be due to a direct reaction of the water with the $\cdot$Si$\equiv$Si$_3$ centers, incorporating the dangling orbital in a bond with hydrogen. The three possibilities are based on the assumption that water can penetrate and hydrate such a thin oxide (at least partially) to the interface.

As the oxidation proceeds, the entire surface is ultimately protected by an oxide of good integrity and strength. The oxide-related O_2 traps become effective as the insulating properties of the oxide improve, and UV bleaching via transport to these traps is initiated. The oxide film at this later stage also provides an effective seal against widespread room-temperature penetration of H_2O to the interface, and the effects of water are confined to the outer oxide trapping region or to pinholes. Thus the ESR signal reappears upon immersion after bleaching.

The nascent oxide observations offer added support for the physical model of UV bleaching proposed above, as contrasted with a chemical model. It might have been postulated, for example, that UV produces a neutralization of the $\cdot$Si$\equiv$Si$_3$ center by a photochemical reaction which is otherwise precluded by energy barriers in the strained oxide region. However, the UV-accelerated development of the nascent oxide ESR signal, corroborated by oxide growth studies elsewhere,[15] makes a similar photochemical explanation for the contrary effect (bleaching) rather unattractive. Thus we favor the physical model above, though additional information would likely improve all explanations offered here.

IV. CONCLUDING REMARKS

The UV experiments show that $\cdot$Si$\equiv$Si$_3$ centers can be controllably discharged by physical means. Moreover, the ESR measurement in this "thin oxide" regime should provide a valuable tool for a much more detailed understanding of the Si/SiO_2 interface and the development of the D_{it} and N_f centers. Thus the clarification of the correct mechanism for the signal variation from the possibilities described above is of considerable interest. Finally, in regard to device application, the interface is shown to have a physico-chemical nature which varies significantly throughout the thin oxide range, perhaps extending to the regime of gate oxides for submicrometer devices.

ACKNOWLEDGMENT

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